Temporal Variations of Ore Mineralogy and Sulfur Isotope Data from the Boguk Cobalt Mine, Korea: Implication for Genesis and Geochemistry of Co-bearing Hydrothermal System

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ABSTRACT : The Boguk cobalt mine is located within the Cretaceous Gyeongsang Sedimentary Basin. Major ore minerals including cobalt-bearing minerals (loellingite, cobaltite, and glaucodot) and Co-bearing arsenopyrite occur together with base-metal sulfides (pyrrhotite, chalcopyrite, pyrite, sphalerite, etc.) and minor amounts of oxides (magnetite and hematite) within fracture-filling quartz±actinolite±carbonate veins. These veins are developed within an epicrustal micrographic granite stock which intrudes the Konchonri Formation (mainly of shale). Radiometric date of the granite (85. 98 Ma) indicates a Late Cretaceous age for granite emplacement and associated cobalt mineralization. The vein mineralogy is relatively complex and changes with time: cobalt-bearing minerals with actinolite, carbonates, and quartz gangues (stages I and II) → base-metal sulfides, gold, and Fe oxides with quartz gangues (stage III) → barren carbonates (stages IV and V). The common occurrence of high-temperature minerals (cobalt-bearing minerals, molybdenite and actinolite) with low-temperature minerals (base-metal sulfides, gold and carbonates) in veins indicates a xenothermal condition of the hydrothermal mineralization. High enrichment of Co in the granite (avg. 50.90 ppm) indicates the magmatic hydrothermal derivation of cobalt from this cooling granite stock, whereas higher amounts of Cu and Zn in the Konchonri Formation shale suggest their derivations largely from shale. The decrease in temperature of hydrothermal fluids with a concomitant increase in fugacity of oxygen with time (for cobalt deposition in stages I and II, T=560°-390°C and log fO_2=>-32.7 to -30.7 atm at 350°C; for base-metal sulfide deposition in stage III, T=380°-345°C and log fO_2=≥-30.7 atm at 350°C) indicates a transition of the hydrothermal system from a magmatic-water domination toward a less-evolved meteoric-water domination. Sulfur isotope data of stage II sulfide minerals evidence that early, Co-bearing hydrothermal fluids derived originally from an igneous source with a $\delta^{34}S_{\Sigma S}$ value near 3 to 5‰. The remarkable increase in $\delta^{34}S_{H2S}$ values of hydrothermal fluids with time from cobalt deposition in stage II (3-5‰) to base-metal sulfide deposition in stage III (up to about 20‰) also indicates the change of the hydrothermal system toward the meteoric water domination, which resulted in the leaching-out and concentration of isotopically heavier sulfur (sedimentary sulfates), base metals (Cu, Zn, etc.) and gold from surrounding sedimentary rocks during the huge, meteoric water circulation. We suggest that without the formation of the later, meteoric water circulation extensively through surrounding sedimentary rocks the Boguk cobalt deposits would be simple veins only with actinolite + quartz + cobalt-bearing minerals. Furthermore, the formation of the meteoric water circulation after the culmination of a magmatic hydrothermal system resulted in the common occurrence of high-temperature minerals with later, lower-temperature minerals, resulting in a xenothermal feature of the mineralization.

INTRODUCTION

The genetic theory of worldwide cobalt-bearing deposits is not yet established. Traditionally, hydrothermal cobalt deposits have been viewed as the products of deposition directly from hydrothermal solution of magmatic origin. Recently however, many cobalt-bearing deposits of non-magmatic hydrothermal origin have been discovered (e.g., Kerrich et al., 1986; Kissin, 1988). In fact, Co

(and Ni) is rare in minerals from ore deposits of magmatic hydrothermal origin owing to its strong partitioning to the magmatic phase (typically, mafic minerals of crystallizing silicate melts) and resulting depletion in residual hydrothermal fluids, as well as due to very low solubility under most hydrothermal conditions (Crerar et al., 1985; Susak, Crerar, 1985). Halls and Stumpfl (1972) compiled the geneses of cobalt deposits and classified them into four genetic groups: magmatic (Badham, 1975 and 1976; Horrall et al., 1993); metamorphic (Kerrich et al., 1986; Goodz et al., 1986); sedimentary syngenetic (Schneider, 1972); and non-magmatic (Kissin, 1988).

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It is interesting that the Boguk cobalt deposits in this study, located in the Gyeongsan city near Taegu, share many features with deposits of the granite-related magmatic hydrothermal origin.

There are few cobalt-bearing deposits in Korea, which can be grouped as two types (Nakamura, 1942): (1) deposits associated with Cu, Zn, Au and Ag mineralization in a genetic tie with felsic igneous rocks; (2) deposits associated with nickel in basic igneous rocks, where cobalt-bearing minerals occur only as a by-product. The Boguk cobalt deposits belong to the first group.

Only a few studies of cobalt deposits in Korea were carried out. Nakamura (1942) briefly summarized the geology and ore deposits of the Boguk cobalt mine. Recently, Park (1990) described the ore mineralogy and mineral chemistry of the cobalt mineralization at Boguk, and suggested the xenothermal origin. However, not only the source and physicochemical conditions of ore mineralization but also the evolution of hydrothermal fluids have not been understood. This study aims to describe the nature of complex ore mineralogy and to decipher the origin of sulfur (and associated metals) and physicochemical conditions of ore mineralization at the Boguk mine, based on mineralogical and geochemical studies, in order to provide a genetic model for the Co-bearing, magmatic hydrothermal system.

GEOLOGIC SETTING

The Boguk cobalt mine area is located within the northern part of the Milyang Subbasin which occupies the southern part of the Cretaceous Gyeongsang Sedimentary Basin. The geology is composed of sedimentary rocks of the Hayang and Yucheon groups and the Bulgugsa Granite (Fig. 1). The Hayang Group rocks of the mine area belong to the Konchonri Formation which consists mainly of shale with minor intercalations of sandstone and limestone. The bedding mainly strikes 320° to 355° and dips 5° to 15° SW. The Yucheon Group rocks extrude or intrude the Konchonri Formation and consist mainly of andesite and andesite porphyry.
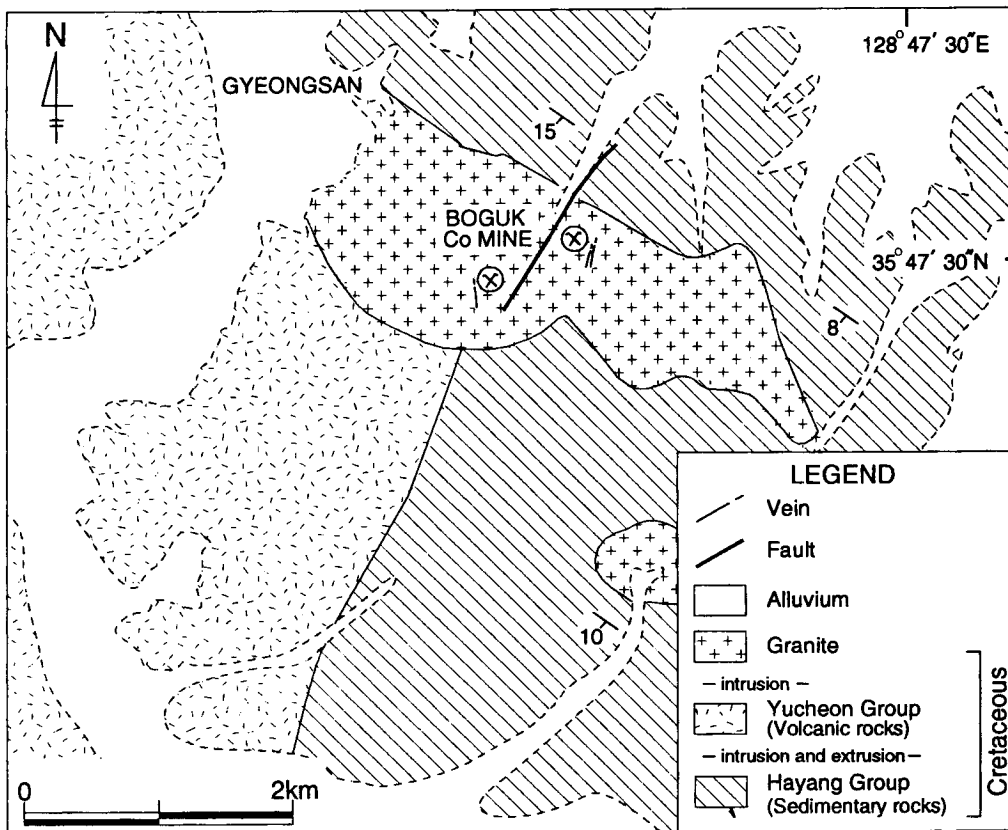

Fig. 1. Local geologic map of the Boguk cobalt mine area.

Table 1. Rb-Sr two-point isochron data of granite from the Boguk cobalt mine area.

Sample no.	Description	^{87}Sr (ppm)	^{87}Rb (ppm)	^{87}Sr/^{86}Sr	^{87}Rb/^{86}Sr	Isochron parameters		Date (Ma)
						Slope ($\times 10^{-3}$)	Intercept	
BK-A	Whole-rock	99.62	158.253	0.7123	4.5889	1.22	0.7067	85.98
	Biotite	12.21	479.162	0.8470	114.8880			

A small granite stock intrudes the Konchonri Formation and hosts fracture-filling hydrothermal veins of the Boguk cobalt mine (Fig. 1). Along the intrusive contacts with sedimentary rocks occurs the intrusion-related prophyllitic alteration. The granite is occasionally uneven in grain size, ranging from fine- to medium-grained. Inward from the margin, the grain size usually increases. The granite also shows miarolitic cavities and micrographic texture. These features imply their epicrustal emplacement and the presence of abundant volatile components in magma. A Rb-Sr age of the granite (85.98 Ma; Table 1) suggests a Late Cretaceous age of the granitic intrusion and possibly the associated ore mineralization.

ORE MINERALOGY

General descriptions

The cobalt mineralization at Boguk consists of narrow (each 0.1~0.5 m thick), fracture-filling hydrothermal quartz + carbonates + actinolite veins. These veins occur within a calc-alkaline, micrographic granite stock which intrudes the volcanosedimentary strata of the Cretaceous Gyeongsang Supergroup. The ore minerals consist of cobalt-bearing minerals (loellingite, cobaltite, and glaucodot), cobalt-rich arsenopyrite, molybdenite, base-metal sulfides (chalcopyrite, sphalerite, pyrite, pyrrhotite, etc.), and rare amounts of oxides (magnetite and hematite).

Based on careful investigation of the mineral assemblages and textural relationships (e. g., cutting, banding, etc.) of veins, along with microscopic study of ore samples, the hydrothermal vein mineralization at Boguk formed during five major mineralization stages (Fig. 2).

During stages I and II, cobalt deposition as loellingite, cobaltite and glaucodot occurred. These cobalt minerals are associated intimately with arsenopyrite, molybdenite and minor amounts of other sulfides (Fig. 3A). Stage I mineralization is characterized by the occurrence of green amphibole (mainly actinolite) in an association with minor quartz and carbonates. Ore minerals consist mainly of loellingite and Co-bearing arsenopyrite with rare amounts of molybdenite, cobaltite, glaucodot, pyrrhotite, etc.; Toward the stage II mineralization, cobalt-

Fig. 2. Generalized paragenetic sequence of hydrothermal minerals from veins and alteration zones of the Boguk cobalt mine.

bearing minerals are generally decreased in amounts, whereas arsenopyrite and other sulfides increased. Stage II mineralization is characterized by the association of cobalt mineralization (solely as loellingite) with clear quartz and the absence of amphibole. Cobaltite-glaucodot solid solution minerals do not occur in this stage. Stage II ore mineralogy consists dominantly of arsenopyrite and loellingite with minor amounts of fine-grained base-metal sulfides such as chalcopyrite, pyrite, sphalerite, pyrrhotite, etc. (Fig. 3B, C).

Stage III mineralization is represented by the deposition of base-metal sulfides without cobalt-bearing minerals, and consists mineralogically of white quartz and carbonates with relatively abundant base-metal sulfides (arsenopyrite, chalcopyrite, sphalerite, pyrite, pyrrhotite, bismuthinite, etc.; Fig. 3D) and oxides (magnetite and hematite). Rare amounts of electrum occur with bismuthinite, native bismuth, and chalcopyrite as fracture-fillings in ore and gangue minerals (Fig. 3E). Toward the later portions of stage III mineralization occurs the assemblage of Fe oxides such as magnetite and hematite (Fig. 3F). Stage IV and V mineralizations are represented by deposition of
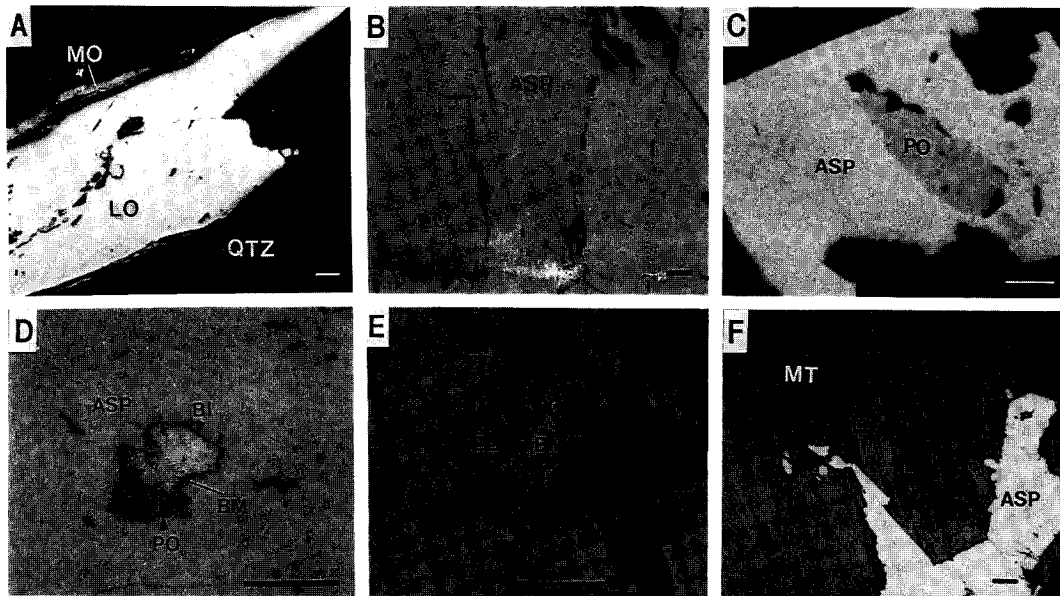
Fig. 3. Reflected light microphotographs of ore mineralization at the Boguk cobalt mine. All scale bars are 0.1 mm. A) Stage I loellingite (LO) and flaky molybdenite (MO). Gangues are quartz (QTZ) and carbonates. B) Stage II loellingite intergrown with arsenopyrite (ASP). C) Stage II subhedral arsenopyrite including pyrrhotite (PO). D) Stage III, native bismuth (BI) + bismuthinite (BM) + pyrrhotite (PO) assemblage in arsenopyrite. E) Stage III, electrum (EL) + bismuthinite + chalcopyrite (CPY) assemblage infilling the fractures or grain margins of arsenopyrite. F) Late stage III, magnetite (MT) and hematite (HM) overgrown to arsenopyrite, indicating the oxidation of hydrothermal fluids.

carbonates with rare sulfides.

The vein mineralogy of the Boguk cobalt mine is relatively complex and tends to be changed with time as follows: actinolite, cobalt-bearing minerals and molybdenite (stages I and II) → base-metal sulfides (stage III) → carbonates (stages IV and V). This mineralogical shift from high-temperature ore minerals (e.g., cobalt-bearing minerals and molybdenite) to low-temperature ore minerals (e.g., base-metal sulfides and gold) suggests the relatively shallow-depth, xenothermal condition of hydrothermal mineralization at Boguk.

Occurrence of arsenopyrite

Arsenopyrite is the most abundant mineral at Boguk and occurs throughout the mineralizations except stage V. Typical occurrences of each stage's arsenopyrite are summarized as follows:

(1) Stage I arsenopyrite occurs usually as discrete grains with subhedral to anhedral forms, and is intimately associated with cobalt-bearing minerals (loellingite, cobaltite, and glaucodot). It also replaces the loellingite, remaining islands of loellingite. Occasionally it contains minute grains of pyrrhotite.

(2) Stage II arsenopyrite occurs as coarse, euhedral

to subhedral aggregates which are intergrown with loellingite, pyrrhotite, and clear quartz (Fig. 3B, C). Occasionally, it shows compositional zoning in a single grain with a variation range up to about 2 atom. % As.

(3) Stage III arsenopyrite occurs as aggregates of fine euhedral grains (up to 0.05 mm) in the early, marginal portions of stage III veins. It is associated with chalcopyrite and pyrite. Characteristically, it often contains blebs of native bismuth and bismuthinite (Fig. 3D). Compared with stage I and II arsenopyrites, it contains lesser amounts of arsenic and cobalt.

(4) Stage IV arsenopyrite occurs as disseminations within carbonate bands. Repeated banding of carbonates in stage IV veins indicates a repeated, sudden change of physicochemical depositional conditions (e.g., boiling or meteoric-water mixing), thus being unable to attain an equilibrium for proper mineral assemblages. Thus, stage IV arsenopyrite cannot be used for a good geothermometer.

CHEMICAL COMPOSITIONS OF ARSENOPYRITE: IMPLICATION FOR THERMOCHEMICAL CONDITIONS

Electron microprobe analyses of arsenopyrites are

Fig. 3. Reflected light microphotographs of ore mineralization at the Boguk cobalt mine. All scale bars are 0.1 mm. A) Stage I loellingite (LO) and flaky molybdenite (MO). Gangues are quartz (QTZ) and carbonates. B) Stage II loellingite intergrown with arsenopyrite (ASP). C) Stage II subhedral arsenopyrite including pyrrhotite (PO). D) Stage III, native bismuth (BI) + bismuthinite (BM) + pyrrhotite (PO) assemblage in arsenopyrite. E) Stage III, electrum (EL) + bismuthinite + chalcopyrite (CPY) assemblage infilling the fractures or grain margins of arsenopyrite. F) Late stage III, magnetite (MT) and hematite (HM) overgrown to arsenopyrite, indicating the oxidation of hydrothermal fluids.

Table 2. Electron microprobe analyses of arsenopyrite from the Boguk cobalt mine.

stage	Specimen no.	Weight percent							Atomic percent					
		Fe	S	As	Sb	Co	Ni	Total	Fe	S	As	Sb	Co	Ni
I	2-86	28.88	16.54	50.63	0.05	4.30	0.00	100.40	29.02	28.95	37.92	0.02	4.09	0.00
	n1-78	26.04	16.40	49.82	0.29	6.80	0.00	99.35	26.48	29.06	37.77	0.14	6.55	0.00
	2L-4	30.22	16.01	50.10	0.15	3.69	0.00	100.17	30.52	28.16	37.71	0.07	3.53	0.00
	35-74	27.82	16.48	50.01	0.00	5.32	0.14	99.77	28.11	29.00	37.66	0.00	5.09	0.13
	11-76	30.51	16.61	50.31	0.00	2.90	0.13	100.46	30.57	28.99	37.57	0.00	2.75	0.12
	n1-79	29.94	16.52	49.35	0.00	2.68	0.20	98.69	30.48	29.29	37.45	0.00	2.59	0.19
	b12-72	32.06	16.73	50.17	0.00	1.66	0.00	100.62	32.00	29.09	37.33	0.00	1.57	0.00
	2-88	29.20	16.90	49.67	0.00	3.81	0.06	99.64	29.40	29.64	37.27	0.00	3.63	0.06
	2-87	28.18	16.77	49.05	0.21	4.42	0.00	98.63	28.68	29.74	37.22	0.10	4.26	0.00
	b12-60	31.08	17.18	49.78	0.01	2.02	0.00	100.07	31.07	29.92	37.09	0.00	1.91	0.00
	a-37	26.81	16.56	49.19	0.10	6.99	0.03	99.68	27.07	29.13	37.03	0.05	6.69	0.03
	35-75	27.38	17.06	49.17	0.08	5.71	0.00	99.40	27.60	29.96	36.95	0.04	5.45	0.00
	n1-80	29.59	16.89	49.47	0.19	4.11	0.00	100.25	29.63	29.46	36.92	0.09	3.90	0.00
	b12-61	31.31	16.91	49.15	0.00	1.99	0.00	99.36	31.53	29.67	36.90	0.00	1.90	0.00
	bk4-18	33.12	16.84	48.73	0.34	0.00	0.16	99.19	33.43	29.60	36.66	0.16	0.00	0.15
	b12-69	31.64	17.26	49.04	0.00	1.76	0.05	99.75	31.65	30.07	36.56	0.00	1.67	0.05
	a-38	25.45	16.72	48.52	0.00	8.75	0.07	99.51	25.68	29.39	36.50	0.00	8.37	0.07
	n1-77	28.90	17.15	48.30	0.00	4.35	0.07	98.77	29.20	30.19	36.38	0.00	4.17	0.07
	2L-2	30.39	17.38	48.42	0.00	3.38	0.00	99.57	30.40	30.29	36.11	0.00	3.20	0.00
	a-42	25.14	16.92	47.67	0.00	8.92	0.00	98.65	25.50	29.89	36.04	0.00	8.57	0.00
	a-41	28.13	17.64	48.62	0.01	5.87	0.00	100.27	27.94	30.52	36.00	0.00	5.53	0.00
	2L-3	30.57	17.28	48.84	0.00	4.29	0.04	101.02	30.21	29.75	35.98	0.00	4.02	0.04
	2L-1	30.30	17.12	48.24	0.00	4.17	0.00	99.83	30.29	29.81	35.95	0.00	3.95	0.00
	b12-67	32.32	18.83	48.30	0.30	0.70	0.04	100.49	31.70	32.17	35.31	0.13	0.65	0.04
	bk2-10	30.62	18.17	47.77	0.00	3.19	0.00	99.75	30.35	31.37	35.29	0.00	3.00	0.00
	bk2-6	31.15	18.68	47.06	0.00	3.03	0.10	100.02	30.62	31.98	34.48	0.00	2.82	0.09
	bk2-4	31.34	19.20	46.46	0.00	2.29	0.12	99.41	30.82	32.89	34.05	0.00	2.13	0.11
	bk2-7	30.96	18.73	45.93	0.08	3.06	0.09	98.85	30.70	32.35	33.95	0.04	2.88	0.08
	mean	29.61	17.20	48.85	0.06	3.93	0.05	99.70	29.67	30.01	36.50	0.03	3.75	0.04
II	n15-17	27.20	16.09	50.46	0.00	6.46	0.29	100.50	27.41	28.24	37.90	0.00	6.17	0.28
	b15-21	28.93	16.71	50.82	0.13	4.14	0.13	100.86	28.92	29.10	37.87	0.06	3.92	0.12
	n4-2	29.77	16.06	50.13	0.00	3.55	0.39	99.90	30.12	28.30	37.80	0.00	3.40	0.38
	n15-16	27.15	16.06	49.02	0.14	5.67	0.06	98.10	27.94	28.79	37.61	0.07	5.53	0.06
	n15-23	26.60	16.15	49.48	0.04	6.76	0.26	99.29	27.06	28.62	37.53	0.02	6.52	0.25
	n15-19	25.73	16.76	49.53	0.12	7.23	0.80	100.17	25.86	29.34	37.10	0.06	6.88	0.76
	n15-31	31.32	16.98	48.93	0.00	1.31	0.07	98.61	31.74	29.97	36.96	0.00	1.26	0.07
	n4-7	29.96	16.80	49.53	0.00	3.96	0.10	100.35	29.96	29.97	36.92	0.00	3.75	0.10
	n4-8	29.66	16.87	49.42	0.00	3.83	0.30	100.08	29.72	29.45	36.91	0.00	3.64	0.29
	n15-36	29.33	16.62	48.52	0.00	4.12	0.12	98.71	29.79	29.40	36.73	0.00	3.97	0.12
	n18-73	31.24	17.28	49.21	0.18	2.01	0.09	100.01	31.21	30.07	36.65	0.08	1.90	0.09
	bk9-22	30.28	17.15	48.26	0.04	2.78	0.02	98.53	30.65	30.24	36.41	0.02	2.67	0.02
	n15-24	29.25	17.35	48.34	0.07	3.62	0.22	98.85	29.49	30.47	36.33	0.03	3.46	0.21
	n15-14	31.51	17.34	47.56	0.20	1.44	0.03	98.08	31.94	30.62	35.94	0.09	1.38	0.03
	n18-71	31.10	17.30	48.22	0.00	3.07	0.00	99.69	31.07	30.11	35.91	0.00	2.91	0.00
	n18-72	31.21	17.73	48.06	0.29	2.17	0.01	99.47	31.17	30.85	35.78	0.13	2.05	0.01
	n4-1	32.48	17.78	48.60	0.18	1.35	0.31	100.70	32.05	30.56	35.75	0.08	1.26	0.29
	n15-33	30.48	17.50	47.48	0.00	2.81	0.05	98.32	30.77	30.77	35.73	0.00	2.69	0.05
	n4-9	30.51	17.61	48.19	0.00	3.66	0.04	100.01	30.32	30.49	35.70	0.00	3.45	0.04
	n15-10	29.66	17.58	47.58	0.11	3.41	0.42	98.76	29.83	30.80	35.67	0.05	3.25	0.40
	bk9-19	30.82	17.93	48.26	0.00	3.07	0.00	100.08	30.53	30.94	35.64	0.00	2.88	0.00
	n18-70	32.56	17.58	47.63	0.14	1.01	0.00	98.92	32.66	30.71	35.61	0.06	0.96	0.00
	n4-10	30.52	17.82	48.22	0.00	3.65	0.16	100.37	30.18	30.70	35.55	0.00	3.42	0.15
	bk9-31	32.41	17.76	47.49	0.02	0.86	0.07	98.61	32.53	31.05	35.53	0.01	0.82	0.07

Table 2. Continued.

stage	Specimen no.	Weight percent							Atomic percent					
		Fe	S	As	Sb	Co	Ni	Total	Fe	S	As	Sb	Co	Ni
II	bk9-20	32.06	18.17	48.17	0.30	1.44	0.08	100.22	31.68	31.28	35.48	0.14	1.35	0.08
	n15-35	31.90	18.04	47.87	0.42	1.50	0.03	99.76	31.69	31.22	35.45	0.19	1.41	0.03
	bk9-27	31.85	17.70	47.28	0.00	1.67	0.16	98.66	31.96	30.94	35.36	0.00	1.59	0.15
	n4-3	29.64	17.83	47.90	0.00	4.67	0.17	100.21	29.35	30.75	35.35	0.00	4.38	0.16
	bk9-24	32.28	17.95	46.96	0.13	0.92	0.00	98.24	32.45	31.43	35.19	0.06	0.88	0.00
	bk9-29	32.25	18.70	47.76	0.00	1.42	0.00	100.13	31.69	32.01	34.98	0.00	1.32	0.00
	bk9-23	31.47	18.15	46.71	0.00	2.31	0.00	98.64	31.44	31.59	34.79	0.00	2.19	0.00
	bk9-28	33.06	18.41	46.91	0.21	0.71	0.00	99.30	32.78	31.79	34.67	0.10	0.67	0.00
	n18-69	31.45	18.55	46.41	0.00	1.67	0.00	98.08	31.47	32.33	34.62	0.00	1.58	0.00
	n18-68	32.25	19.00	46.18	0.00	0.77	0.00	98.20	32.09	32.93	34.25	0.00	0.73	0.00
	bk9-21	31.87	18.52	46.21	0.10	2.47	0.06	99.23	31.55	31.94	34.10	0.05	2.32	0.06
	n18-67	32.78	19.59	46.29	0.15	2.38	0.11	101.30	31.57	32.86	33.23	0.07	2.17	0.10
	mean	30.63	17.54	48.16	0.08	2.89	0.13	99.42	30.63	30.55	35.92	0.04	2.74	0.12
III	n21-84	32.86	18.15	48.47	0.00	0.37	0.00	99.85	32.55	31.32	35.79	0.00	0.35	0.00
	7L-5	33.59	17.41	47.22	0.00	0.00	0.00	98.22	33.89	30.60	35.51	0.00	0.00	0.00
	n21-82	33.09	17.98	47.74	0.28	0.09	0.08	99.26	33.00	31.23	35.48	0.13	0.09	0.08
	n21-81	32.88	18.00	47.46	0.00	0.01	0.15	98.50	32.96	31.43	35.46	0.00	0.01	0.14
	7L-11	33.68	17.57	47.07	0.00	0.18	0.04	98.54	33.82	30.73	35.23	0.00	0.17	0.04
	7L-11	30.62	17.83	47.13	0.15	2.97	0.03	98.73	30.71	31.15	35.23	0.07	2.82	0.03
	7L-12	33.90	18.07	47.36	0.04	0.01	0.00	99.38	33.66	31.26	35.05	0.02	0.01	0.00
	7L-9	33.05	18.31	46.82	0.06	0.09	0.04	98.37	33.05	31.90	34.90	0.03	0.09	0.04
	7L-6	33.72	17.91	46.70	0.00	0.00	0.20	98.53	33.75	31.22	34.84	0.00	0.00	0.19
	n21-85	32.33	18.86	46.64	0.00	0.66	0.00	98.49	32.15	32.67	34.57	0.00	0.62	0.00
	n21-83	34.24	20.05	47.16	0.00	0.03	0.06	101.54	32.80	33.45	33.67	0.00	0.03	0.05
	7L-8	34.67	20.77	45.29	0.15	0.22	0.00	101.10	33.05	34.49	32.19	0.07	0.20	0.00
	7L-4	34.95	20.82	43.55	0.00	0.00	0.00	99.32	33.71	34.98	31.31	0.00	0.00	0.00
	mean	33.35	18.59	46.82	0.05	0.36	0.05	99.22	33.01	32.03	34.56	0.02	0.34	0.04

shown in Table 2. Arsenopyrites from the Boguk mine show wide compositional variations in terms of As content. These wide compositional ranges have been interpreted as effects of variations in temperature and/or sulfur fugacity of hydrothermal fluids (e.g., Lowell, Gasparini, 1982; Kalogeropoulos, 1984). Our analytical data are plotted into a central portion in the (Fe+Co)-As-S triangle diagram (Fig. 4) and show that arsenopyrites from Boguk typically have the high-temperature, As-excess but S-deficient features.

Equilibrium thermodynamics were applied to estimate the changes in physicochemical conditions of hydrothermal fluids. Experiments by Clark (1960a, b) have shown that buffered arsenopyrite will be enriched in arsenic with increasing temperature but enriched in sulfur with increasing pressure. Kretschmar, Scott (1976), however, proposed the minimal effect of pressure on composition and stressed the applicability of arsenopyrite as a geothermometer in the low-pressure region if the content of minor elements (Co+ Ni) does not exceed 1 wt.%. Most arsenopyrites at Boguk have quite high cobalt contents (more than 1 wt.%). The cobalt content shows a systematic
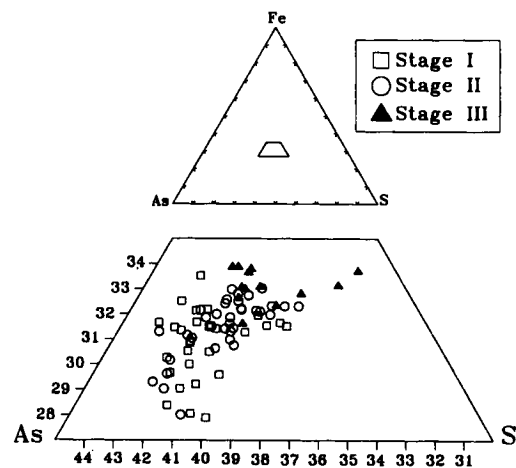

Fig. 4. Enlarged quadrangle in the Fe-As-S compositional triangle, showing the variation of As/S atomic ratio of arsenopyrite from the Boguk cobalt mine.

substitutional relationship with the Fe content, and tends to be decreased toward later mineralization
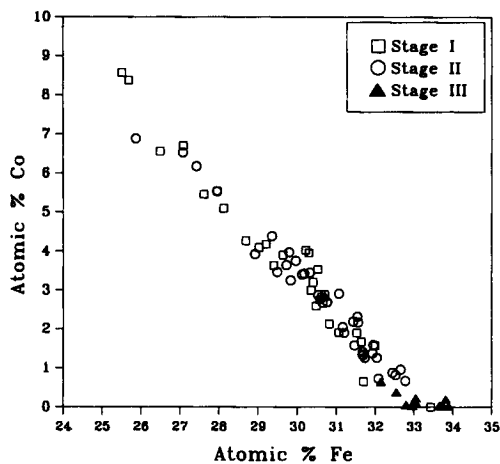
Fig. 5. Fe content versus Co content diagram showing the substitutional relation of arsenopyrites from the Boguk cobalt mine. The cobalt content tends to be decreased toward later mineralization stages.

stages (Fig. 5). Therefore, some arsenopyrites with the Co content of <1 wt.% were used to estimate the temperature, although this approach may not yield the whole range of formation temperatures.

The temperature versus fugacity of sulfur (fS_2) diagram (Kretschmar, Scott, 1976; Fig. 6) was constructed to trace the physicochemical conditions of the Boguk hydrothermal fluids with time.
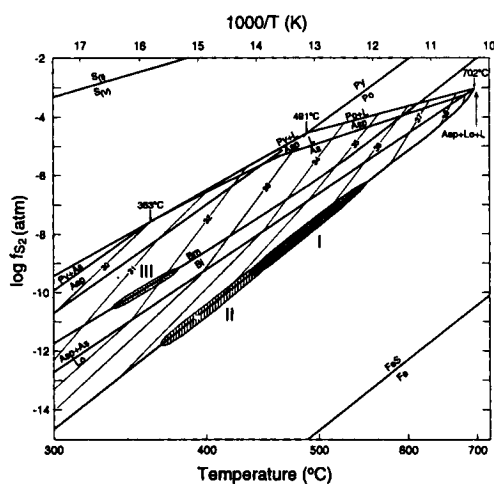
Fig. 6. Temperature versus fugaciy of sulfur diagram (after Kretschmar, Scott, 1976) showing the probable conditions of stage I, II and III mineralizations at Boguk. The bismuth-bismuthinite buffer curve (Barton, Skinner, 1979) is superimposed. Abbreviations: As=native arsenic, Asp= arsenopyrite, Bi=bismuth, Bm=bismuthinite, L=liquid, Lo= loellingite, Po=pyrrhotite, Py=pyrite.

Stage I arsenopyrites (applicable range of As content=35.31 to 36.66 atom.%) are intergrown with loellingite and pyrrhotite. This corresponds to the temperature and log fS_2 values of about 560° to 450°C and -6.5 to -9.5 atm, respectively (Fig. 6). Stage II arsenopyrites coexisting with loellingite and pyrrhotite have the applicable arsenic content of 34.25 to 35.53 atom.%, corresponding to the temperatures of 475° to 390°C and the log fS_2 values of -8.5 to -12.3 atm. Thus, the cobalt deposition (mainly as loellingite) in stages I and II occurred at high temperatures ranging from 390° to 560°C. This high-temperature condition (up to 560°C) indicates that early cobalt mineralization at Boguk formed from cooling magmatic fluids, as also supported by sulfur isotope and lithochemical data (see below).

Stage III arsenopyrite often contains the inclusions of native bismuth and bismuthinite. As shown in Fig. 6, the Bi-Bi$_2$S$_3$ sulfur-buffer univariant curve lies within the arsenopyrite stability field and intersects the compositional isopleths of arsenopyrite at sufficiently high angle, constituting a potentially useful geothermometer. Since each isopleth of arsenopyrite is univariant at a definite pressure, their intersections with the Bi-Bi$_2$S$_3$ curve are invariant and define not only the temperature but also the fS_2 in spite of the absence of any coexisting Fe-S minerals (Kretschmar, Scott, 1976). Arsenic contents of stage III arsenopyrites containing the blebs of native bismuth and bismuthinite range from 31.31 to 32.19 atom.%, corresponding to temperature and log fS_2 values of 345° to 380°C and -9.3 to -10.5 atm, respectively. It is noteworthy that the deposition of base-metal sulfides in stage III occurred from fluids with quite lower temperatures than earlier cobalt mineralization, suggesting the overall cooling of the hydrothermal system with increasing time, possibly due to relatively increasing amounts of meteoric water influx.

It is further possible to define chemical changes responsible for mineral deposition by using a fugacity of sulfur (fS_2) versus fugacity of oxygen (fO_2) diagram (Fig. 7). The diagram, for convenience, has been constructed for 350°C in order to compare the depositional conditions between cobalt mineralization (stages I and II) and base-metal sulfides deposition (stage III). Actual temperature variations between these stages result in positional changes of the mineral equilibria but do not affect the overall topological shape of the diagram. The occurrence of pyrrhotite but the absences of graphite and magnetite in stages I and II allow the permissible range of log fO_2 values between >-32.7 and -30.7 atm, whereas the assemblage pyrite + magnetite ± hematite
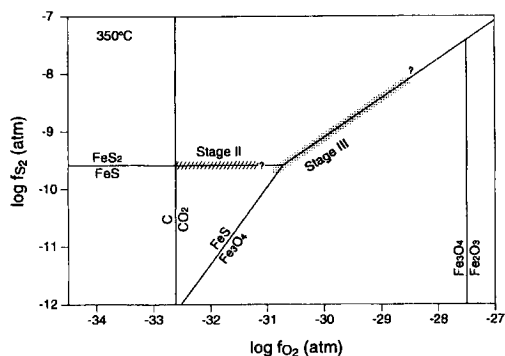
Fig. 7. Fugacity of sulfur versus fugacity of oxygen diagram constructed at 350°C, showing stability relationships of stage II and III mineralizations at Boguk.

$\pm$ pyrrhotite in stage III yields the higher log fO_2 value ($\geq$-30.7 atm). Relatively higher fugacity of oxygen for later, base-metal sulfide mineralization (stage III) also suggests the inundation of more oxidizing, meteoric groundwaters in the hydrothermal system.

LITHOCHEMICAL DATA: IMPLICATION FOR METAL SOURCE

In order to elucidate the potential source(s) of metal components in hydrothermal fluids, surrounding rocks (granite and shale) from the Boguk cobalt mine area were analyzed for trace metallic elements using Inductively Coupled Plasma Mass Spectrometry (Model VGPQLL+) at laboratory in the Korea Basic Science Institute (Table 3).

Compared with worldwide average granite and granodiorite (4 ppm Co; Geological Survey of Finland, 1992) and other Korean Cretaceous granites (13 ppm Co; Hong, 1987), the micrographic granite stock in the Boguk mine area is quite highly enriched in Co (25.08-112.02 ppm, avg. 50.90 ppm), as shown in Fig. 8. The Konchonri Formation shale contains relatively higher amounts of Co (avg. 34.30 ppm), Cu (avg. 89.67 ppm), and Zn (avg. 135.87 ppm) than average worldwide shale (Co=20 ppm, Cu =45-50 ppm, Zn=100 ppm; Levinson, 1974; Geological Survey of Finland, 1992).

Very high cobalt content in the granite indicates that cobalt was probably derived largely from cooling granite stock, whereas higher amounts of Cu and Zn in shale suggest their derivations mainly from shale. Thus, Cu and Zn were probably originated through leaching-out from shale by circulating meteoric water after the culmination of an earlier, cobalt-depositing magmatic hydrothermal system with

temperatures up to 560°C (based on arsenopyrite geothermometry).

SULFUR ISOTOPE DATA: IMPLICATIONS FOR SOURCE AND EVOLUTION OF HYDROTHERMAL FLUIDS

In order to elucidate the origin and evolution of sulfur (and associated metals) in hydrothermal fluids, we analyzed sulfur isotope composition of 10 sulfides from stage II and IV veins (Table 4). Standard techniques for gas extraction and analysis were used (Grinenko, 1962), and isotopic data are reported in δ notation relative to the Canyon Diablo Troilite (CDT) standard. The standard error of analysis is about $\pm 0.1‰$.

Ranges of measured $\delta^{34}S$ values are: sulfides from stage II vein, 3.46 to 6.87‰ (molybdenite=3.46~ 4.82‰; pyrite=6.05‰; arsenopyrite=6.87‰); sulfides from stage IV vein, 11.13 to 21.90‰ (pyrite=17.81~ 21.90‰; chalcopyrite=11.13-19.87‰). To our knowledge, the $\delta^{34}S$ values for stage IV sulfide minerals (up to 21.90‰) are highest among sulfides from hydrothermal vein deposits in Korea.

Assuming appropriate depositional temperatures for each mineral species (based on average homogenization temperatures of fluid inclusions in associated quartz and on thermochemical calculations), the following $\delta^{34}S$ values of H_2S are calculated using the sulfur isotope fractionation equations in Ohmoto and Rye (1979): for stage II, 2.71 to 5.22‰; for stage IV, 11.37 to 20.10‰.

Within stage II, small variations of calculated $\delta^{34}S_{H2S}$ values at high temperatures and the prevalences of both the Fe mineral assemblage pyrrhotite $\pm$ pyrite in veins and the alteration mineral assemblage sericite+quartz likely indicate the predominance of H_2S (and some HS⁻) among dissolved sulfur species in early, cobalt-depositing fluids (Ohmoto, 1972; Ohmoto, Rye, 1979). Ohmoto and Rye (1979) have shown that a magmatic fluid phase in equilibrium with a hydrous granitic melt (log fO_2=-12 atm, pressure=1000 bars, temperature= 800°C, initial $\delta^{34}S_{melt}$ values near 0‰) will have a $\delta^{34}S_{fluid}$ value near 4‰. Therefore, the calculated $\delta^{34}S_{H2S}$ values (about 3 to 5‰) may be taken as an approximation of the sulfur isotope composition of entire, early hydrothermal fluids ($\delta^{34}S_{\Sigma S}$). It is tempting to indicate that the sulfur in early hydrothermal fluids at Boguk was derived originally from an igneous source, likely the vein-hosting granitic stock (Ohmoto, Rye, 1979). Abnormally high $\delta^{34}S_{H2S}$ values (approaching 20‰) for stage IV fluids rule out the significant contribution of an igneous sulfur

Table 3. Metallic element conecentrations (ppm) of granite and shale from the Boguk cobalt mine area.

Sample	granite												shale				
	BK-A	BK-B	BK-C	BK-D	BK-E	BK-F	BK-G	BK-H	BK-I	BK-NA	Mean	Worldwide*	BK2-1	BK2716L	BK2909	Mean	Worldwide**
Cr	8.62	10.95	5.43	5.63	7.50	8.00	10.39	6.80	3.95	4.68	7.20	10	94.00	129.10	165.00	129.70	100
Ni	4.63	4.03	4.00	4.55	4.52	4.43	6.51	4.21	4.32	3.57	4.49	5	63.90	84.30	79.00	75.73	70
Co	59.97	59.69	46.91	49.96	25.08	29.72	112.02	29.13	56.74	39.75	50.90	4	25.50	36.50	40.90	34.30	20
Sc	5.97	5.37	5.43	5.63	7.50	8.00	10.39	6.80	3.95	4.68	6.37	5	36.20	50.70	41.30	42.73	15
Cu	7.47	4.96	13.43	7.54	8.77	6.09	6.43	7.71	4.92	4.52	7.18	12	56.40	64.50	148.10	89.67	45
Pb	13.17	11.42	12.56	15.32	11.37	9.23	10.75	15.01	12.43	15.80	12.71	20	15.70	12.10	21.40	16.40	22
Zn	23.48	30.57	25.36	35.26	31.66	23.69	23.92	40.70	17.59	18.67	27.09	50	88.10	142.00	177.50	135.87	100
Cd	0.39	0.54	0.51	0.48	0.36	0.38	0.28	0.44	0.32	0.56	0.43	0.1	0.50	0.60	0.70	0.60	0.25
Mo	1.15	1.19	1.32	1.70	2.14	1.07	1.51	1.23	1.37	1.49	1.42	1.5	0.60	7.00	27.70	11.77	2.0
Te	0.10	0.28	0.39	0.29	0.02	0.43	0.44	1.45	0.45	0.47	0.43	5	18.10	1.10	8.90	9.37	9
Rb	139.55	177.44	142.59	192.01	197.30	141.34	189.40	171.55	158.05	108.81	161.80	120	109.10	143.10	226.40	159.53	140
Cs	0.79	1.63	1.00	1.99	1.08	1.05	1.28	1.29	0.92	1.31	1.23	4	2.30	3.80	4.90	3.67	5
Ba	726.87	703.21	626.34	636.70	803.73	571.11	742.87	784.01	682.01	678.54	695.54	600	237.10	155.90	559.10	317.37	550
Sr	129.72	87.22	114.75	107.41	148.40	139.73	162.87	160.42	100.45	120.31	127.13	220	960.20	55.50	495.20	503.63	250
Ga	49.57	46.14	44.35	50.49	72.58	59.79	81.87	62.65	56.95	52.20	57.66	18	109.50	78.80	273.00	153.77	20
Li	26.18	29.03	24.58	28.24	55.30	26.43	32.44	37.29	21.30	20.58	30.14	30	249.40	331.80	140.70	240.63	60
Hf	1.25	1.33	2.83	1.93	3.06	0.94	1.77	2.13	3.85	1.15	2.02	5	0.50	2.50	2.20	1.73	4
Zr	28.79	38.45	62.70	48.82	62.57	27.12	57.84	27.02	72.74	27.42	45.35	200	39.10	122.70	130.60	97.47	160
Y	34.25	32.69	29.60	36.35	25.81	28.77	34.01	47.59	24.49	35.91	32.95	35	25.00	35.70	30.50	30.40	30
Th	19.59	17.48	18.32	20.25	14.87	13.72	18.24	19.27	21.26	25.79	18.88	15	7.60	14.50	11.80	11.30	12
Be	2.80	2.48	3.87	3.27	2.91	2.93	3.22	2.52	2.80	3.87	3.07	5	6.80	5.30	5.80	5.97	3

* Average contents of worldwide granites and granodiorites
** Average contents of worldwide shales and schists (data from Geological Survey of Finland, 1992)
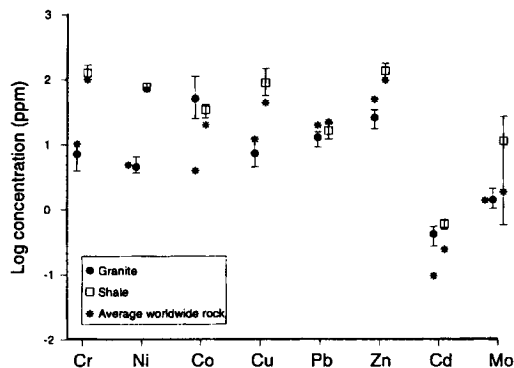
Fig. 8. Concentrations (ppm) of trace metallic elements in granite and shale from the Boguk cobalt mine area. For comparison, average abundances in worldwide granite and granodiorite and shale (after Geological Survey of Finland, 1992) are shown.

Fig. 9. Calculated sulfur isotope composition of H_2S in hydrothermal fluids for the Boguk cobalt mine.

during the stage IV mineralization.

The apparent increase in $\delta^{34}S_{H2S}$ values with time from stage II (avg. 3.73‰) to stage IV (avg. 16.81‰) is noteworthy (Fig. 9). This variation can be explained by some causes: (1) gradual addition of sulfur from an isotopically heavy source, (2) isotopic reequilibration in the hydrothermal fluids following removal of isotopically lighter H_2S by boiling (reservoir effect), and (3) an original isotopically heavy sulfur source (at least 20‰) with an increasing H_2S/sulfate ratio (reduction of sulfur). The case (3) seems unlikely because the observed mineralogical shift of Fe minerals from pyrrhotite±pyrite (stages I and II) to pyrite + magnetite±hematite (stages III and IV) suggests the progressive oxidation of hydrothermal fluids, as discussed above. Therefore, we prefer the cases (1) and (2).
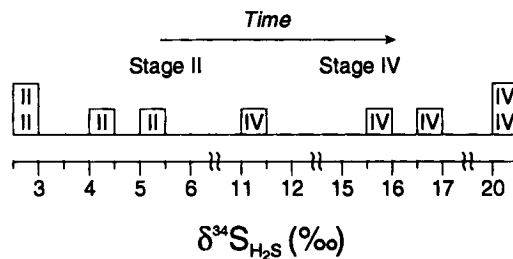
For the case (1), the amounts of introduction of isotopically heavy sulfur (sulfates) from surrounding rocks (possibly the Konchonri Formation sedimentary rocks) must have increased with time from stage II toward stage IV (Hoefs, 1987). It is probable that isotopically heavier sulfur was leached from sedimentary rocks and mixed with minor amounts (if present) of more ^{34}S-depleted igneous sulfur during the formation of a huge circulation of meteoric water after the culmination of an earlier, magmatic hydrothermal system. In addition to the introduction of sulfate-sulfur, base metals such as Cu and Zn were leached out during the meteoric water circulation through sedimentary rocks (see the previous section).

The case (2) is also plausible at Boguk. For stage IV mineralization, characteristic vein textures and mineralogy (e.g., rhythmic banding with abundant carbonates, and occurrence of chalcedonic quartz) suggest the prevalence of boiling of hydrothermal fluids. Drummond and Ohmoto (1985) have shown that with only 5% boiling at 300°C occur the dramatic changes of fluids, including the decrease of ΣH_2S and the increase of pH. Through boiling, H_2S

Table 4. Sulfur isotope data of vein sulfides from the Boguk cobalt mine.

Stage	Sample no.	Mineral	$\delta^{34}S$ (‰)	$\Delta^{34}S$ (‰)	T (°C)*	T (°C)**	$\delta^{34}S_{H2S}$ (‰)***
II	BK-B3	molybdenite	3.73			470	2.92
	BK-B6	molybdenite	4.82			500	4.07
	BK-B8	molybdenite	3.46			500	2.71
	BK-18	arsenopyrite	6.87			-	-
	BK-20	pyrite	6.05			420	5.22
IV	BK-P7	pyrite	21.90			197	20.09
				2.03	197±45		
	BK-P7	chalcopyrite	19.87			197	20.10
	BK-P10	pyrite	18.85			180	16.90
	BK-P13	pyrite	17.81			150	15.58
	BK-P15	chalcopyrite	11.13			180	11.37

* Based on sulfur isotope fractionation equation in Ohmoto and Rye (1979)
** Based on fluid inclusion temperatures, sulfur isotope temperatures, and paragenetic constraints
*** Calculated H_2S isotope compositions based on sulfur isotope fractionations in Ohmoto and Rye (1979)

loss (accompanying the preferential loss of ^{32}S) and isotopic reequilibration, isotopically heavier H_2S can be generated. However, very high enrichment of heavy sulfur (up to $\delta^{34}S_{H_2S}$ values of about 20‰) cannot be explained solely by the boiling. Thus, we prefer the case (2) as an adequate explanation.

CONCLUSIONS AND DISCUSSIONS

Cobalt-bearing, hydrothermal quartz±carbonate± actinolite vein deposits of the Boguk mine fill the fractures in a small micrographic granite stock (Rb-Sr age=85.98 Ma). This granite intrudes the Konchonri Formation rocks (mainly of shale and sandstone) and shows the features implying its epicrustal emplacement. Chemical analyses of rocks show that the granite stock is characteristically highly enriched in Co (avg. 50.90 ppm). This indicates that cobalt was derived from cooling granitic stock. However, quite high concentrations of Cu (avg. 89.67 ppm) and Zn (avg. 135.87 ppm) in the Konchonri Formation shale suggest their derivations largely from shale.

The mineralization of the Boguk cobalt mine is divided into five stages, based on mineral assemblages and textural relationships. The vein mineralogy is relatively complex and changes with increasing paragenetic time: cobalt-bearing minerals including loellingite, cobaltite and glaucodot and molybdenite (in stages I and II) → base-metal sulfides and Fe oxides (in stage III) → carbonates (in stages IV and V). Equilibrium thermodynamic considerations of available mineral assemblages in each stage yield the following physicochemical conditions: (1) cobalt deposition in stages I and II: T=560°-390°C, log fS_2=-6.5 to -12.3 atm, log fO_2 at 350°C=>-32.7 to -30.7 atm; (2) base-metal sulfide deposition in stage III: T=380°-345°C, log fS_2=-9.3 to -10.5 atm, log fO_2 at 350°C=≥-30.7 atm. The progressive decrease in temperature and apparent concomitant increase in fO_2 are interpreted to indicate the progressive inundation of an early, magmatic hydrothermal system for the cobalt mineralization by cooler, more oxidizing meteoric waters during the base-metal sulfide mineralization. The chloro complexing of cobalt ($CoCl_4^{2-}$) is favored as a transporting agent in most hydrothermal conditions (Susak, Crerar, 1985). Precipitation of cobalt from the complexing possibly resulted from the boiling and associated rapid heat loss which occurred due to the pressure drop, as the carbonates associated with cobalt deposition at Boguk could be precipitated in respond to the CO_2 loss and associated pH increase accompanied by the boiling (Kerrich et al., 1986).

The calculated $\delta^{34}S_{H_2S}$ values increase with time

from stage II (3 to 5‰) to stage IV (up to about 20‰). Combined with lithochemical data and equilibrium thermodynamic considerations, these $\delta^{34}S_{H_2S}$ values clarify the ideas that the sulfur in the early, cobalt-depositing hydrothermal fluid was derived from an igneous source, likely the ore-hosting micrographic granitic stock, whereas the sulfur in later fluids for base-metal sulfide mineralization was originated by leaching of isotopically heavier sulfates in sedimentary rocks (the Konchonri Formation) during the lateral circulation of meteoric groundwater. This groundwater circulation system formed after the culmination of the magmatic hydrothermal system which was probably dominated by the vertical fluid flow restrictedly within or around the cooling granitic stock.

Based on the preceding discussions, the following model is proposed for ore genesis at Boguk: During the Late Cretaceous, a micrographic granite stock intruded volcanosedimentary rocks in the Gyeongsang Basin at near surface. Cobalt was partitioned preferentially into a coexisting magmatic hydrothermal fluid. In addition to the actinolite association with cobalt-bearing minerals, sulfur isotope analyses of sulfide minerals in the cobalt mineralization at high temperatures (560° to 390°C) indicate an igneous source of sulfur with a $\delta^{34}S_{\Sigma S}$ value near 3 to 5‰. Following cobalt deposition from a magmatic fluid, a huge circulation of meteoric groundwaters formed to result in cooling, dilution, and oxidation of the early hydrothermal fluids. Base metals (Cu, Zn, etc.) and possibly gold were leached from surrounding sedimentary rocks (Konchonri Formation) during the meteoric water circulation, and were concentrated to form later hydrothermal fluids with lower temperatures and higher $\delta^{34}S$ values. Without the formation of later meteoric water circulation system, the mineralization at Boguk would be simple only with Co-bearing, stage I and II veins.

ACKNOWLEDGEMENTS

REFERENCES

Badham, J.P.N. (1975) Mineralogy, paragenesis and origin of the Ag-Ni, Co arsenide mineralization, Camsell River, N.

W.T. Canada. Miner. Deposita, v. 10, p. 153-175.

Badham, J.P.N. (1976) Orogenesis and metallogenesis with reference to the silver-nickel-cobalt-arsenide ore association, in Strong, D.F. ed., Metallogeny and Plate Tectonics. Geol. Assoc. Can., Spec. Pap. v. 14, p. 541-548.

Barton, P.B. Jr. and Skinner, B.J. (1979) Sulfide mineral stabilities, in Barnes, H.L. ed., Geochemistry of Hydrothermal Ore Deposits (2nd ed.). New York, Wiley, Intersci., p. 278-403.

Clark, L.A. (1960a) The Fe-As-S system: phase relations and applications. Econ. Geol. v. 55, p. 1345-1381.

Clark, L.A. (1960b) The Fe-As-S system. Variations of arsenopyrite compositions as a function of T and P. Carnegie Inst. Wash. Year Book 59, p. 127-130.

Crerar, D.A., Wood, S., Brantly, S. and Bocarsly, A. (1985) Chemical controls on solubility of ore-forming minerals in hydrothermal solutions. Can. Mineral., v. 23, p. 333-352.

Drummond, S.E. and Ohmoto, H. (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems. Econ. Geol., v. 80, p. 126-147.

Geological Survey of Finland (1992) The Geochemical Atlas of Finland, Part 2: till.

Goodz, M.D., Watkinson, D.H., Smejkal, V. and Pertold Z. (1986) Sulfur-isotope geochemistry of the silver-sulfarsenide vein mineralization, Cobalt, Ontario. Can. J. Earth Sci., v. 23, p. 1551-1567.

Grinenko, V.A. (1962) Preparation of sulfur dioxide for isotopic analysis. Zeitschr. Neorgan. Khimii., v. 7, p. 2478-2483.

Halls, C. and Stumpfl, E.F. (1972) The five-element (Ag-Bi-Co-Ni-As) vein deposits - A critical appraisal of the geological environments in which it occurs and of the theories affecting its origin (abs.). 24th Intl. Geol. Congre., Montreal, Sect. 4, p. 540.

Hoefs, J. (1987) Stable isotope geochemistry (3rd ed.). Berlin, Springer-Verlag, 241p.

Hong, Y.K. (1987) Geochemical characteristics of Precambrian, Jurassic and Cretaceous granites in Korea. Jour. Korean Inst. Mining Geol., v. 20, p. 35-60.

Horrall, K.B., Hagni, R.D. and Kisvarsanyi, G. (1993) Mafic and ultramafic plutons associated with the New Madrid Rift Complex-A possible major source of the copper-cobalt-nickel mineralization of southeast Missouri. Econ. Geol., v. 88, p. 328-343.

Kalogeropoulos, S.I. (1984) Composition of arsenopyrite from the Olympias Pb-Zn massive sulfide deposit, Chalkidiki Peninsula, N. Greece. Neues Jahrb. Mineral. Monatsh., p. 296-300.

Kerrich, R., Strong, D.F., Andrews, A.J. and Owsiacki, L. (1986) The silver deposits at Cobalt and Gowganda, Ontario: III. Hydrothermal regimes and source reservoirs - evidence from H.O.D. and Sr isotopes and fluid inclusions. Can. J. Earth Sci., v. 23, p. 1519-1550.

Kissin, S.A. (1988) Nickel-cobalt-native silver (five-element) veins: A rift-related ore type, in Kisvarsanyi, G. and Grant, S.K., eds., Proc. North Am. Conf. on Tectonic Control of Ore Deposits and the Vertical and Horizontal Extent of Ore Systems. Univ. Missouri-Rolla, Rolla, Mo., p. 268-279.

Kretschmar, U. and Scott, S.D. (1976) Phase relations involving arsenopyrite in the system Fe-As-S and their application. Canadian Mineralogist, v. 14, p. 364-386.

Levinson, A.A. (1974) Introduction to Exploration Geochemistry. Applied Publishing Ltd., Calgary.

Lowell, G.R. and Gasparrini, C. (1982) Composition of arsenopyrite from topaz greisen veins in southeastern Missouri. Mineral. Deposita, v. 17, p. 229-238.

Nakamura, K. (1942) A report of Korean cobalt mine. Jour. Geol., v. 49, no. 585, p. 218-220 (in Japanese).

Ohmoto, H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol., v. 67, p. 551-578.

Ohmoto, H. and Rye, R.O. (1979) Isotopes of sulfur an carbon, in Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits (2nd ed.). New York, Wiley Intersci., p. 509-567.

Park, M.E. (1990) Mineralization and paragenesis of the cobalt-bearing sulfide and arsenide minerals in Gyeongsan area. Jour. Geol. Soc. Korea, v. 26, p. 18-31 (in Korean).

Schneider, H.J. (1972) Stratabound polymetallic and Fe-Ba deposits of the Sarrabus-Gerrei region, southeastern Sardinia: I. Mineral deposits and geology. Neues Jahrb. Mineral., Monatsh., v. 12, p. 529-541 (in German).

Susak, N.J. and Crerar, D.A. (1985) Spectra and coordiantion changes of transition metals in hydrothermal solution: Implications for ore genesis. Geochim. Cosmochim. Acta, v. 49, p. 555-564.

보국 코발트 광상의 산출 광물종 및 황동위원소 조성의 시간적 변화: 함코발트 열수계의 성인과 지화학적 특성 고찰

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요   약 : 보국 코발트 광산은 백악기 경상분지내에 위치하며, 셰일로 구성된 건천리층을 천부 관입한 암주상의 미문상 화강암내에 국한하여 배태된다. 광상은 열극 충진형 석영±액티놀라이트±탄산염 광물맥으로 이루어지며, 광석광물로는 함코발트광물 (비독사석, 휘코발트석, 글로코도트), 함코발트 유비철석과 소량의 황화광물 (자류철석, 황동석, 황철석, 섬아연석) 및 미량의 산화광물 (자철석, 적철석)이 산출된다. Rb-Sr 절대연령 측정 결과, 화강암의 관입 및 이와 관련된 광화작용은 후기 백악기 (85.98 Ma)에 이루어진 것으로 판단된다. 산출광물종은 다소 복잡한 양상을 보이며, 시간에 따라 다음과 같이 변화한다: 액티놀라이트, 탄산염광물 및 석영에 수반되는 함코발트 광물의 정출 (광화시기 I, II) → 석영에 수반되는 황화광물, 금 및 산화광물의 정출 (광화시기 III) → 탄산염광물의 정출 (광화시기 IV, V). 고온성 광물 (함코발트 광물, 휘수연석, 액티놀라이트)과 더불어 저온성 광물 (황화광물, 금, 탄산염광물)이 산출되는 점으로 보아 열수광화작용은 xenothermal 환경에서 형성되었다. 화강암은 특징적으로 높은 코발트 함유량 (평균 50.90 ppm)을 나타내며, 이는 코발트가 냉각하는 화강암 암주에서 기원하였음을 지시한다. 반면, 건천리층 셰일의 높은 동 및 아연 함유량은 이들 원소가 주로 셰일로부터 유래되었음을 지시한다. 열수용액의 온도 감소와 더불어 산소분압이 감소 (광화 I, II기의 코발트광물 형성, T=560°-390℃, log fO₂=>-32.7 to -30.7 atm at 350℃; 광화 III기의 황화광물 형성, T=380°-345℃, log fO₂=≥-30.7 atm at 350℃)함은 열수계가 시간이 지남에 따라 초기 마그마성 계로부터 천수로 지배되는 열수계로 전이되었음을 나타낸다. 광화 II기의 유황 동위원소 값은 초기 함코발트 열수 용액이 화성기원 (δ³⁴S_ΣS≅3-5‰)으로부터 기원하였음을 증거한다. 열수용액의 δ³⁴S_H₂S 값은 광화 II기의 코발트 형성기 (3-5‰)로부터 황화광물 형성 시기인 광화 IV기 (최대 약 20‰)까지 크게 증가하였다. 이는 후기로 갈수록 천수가 우세한 열수계로 진화하면서 주위의 퇴적암을 순환하는 과정에 동위원소적으로 무거운 유황 (퇴적기원의 황산염)과 천금속 (Cu, Zn 등) 및 금을 용해, 농집시켰음을 시사한다. 후기에 천수의 유입이 없었더라면, 보국 광상은 단순히 액티놀라이트 + 석영 + 함코발트 광물로 구성된 광맥으로만 형성되었을 것이다. 또한, 마그마 기원의 열수계가 형성된 이후에 천수 순환계가 형성됨으로 인하여 고온 광물과 저온 광물이 함께 산출되는 xenothermal 한 광상의 특성을 나타내게 되었다.